SENSITIZED FLUORESCENCE*

THIRD

SEMIANNUAL TECHNICAL

SUMMARY REPORT

1 July 1964 through 31 December 1964

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ABSTRACT

Another technique for the determination of the total quenching cross section of thallium on mercury fluorescence is described. Results from a single run using this method are compared to previously described results. Ways of improving the method are outlined and plans for the direction of experimental work for the next quarter are given.

Additional progress has been made in the past six months on the measurement of the total quenching cross section for mercury 2537 A resonance radiation by thallium. During this time the source has been changed to a "Pen-Ray" 11SC-1 lamp excited by a 60 cps current and maintained at a constant temperature with a water cooled jacket.

Measurements of the fluorescent 2537 A radiation from mercury only cells and from mercury-thallium cells have been made and analyzed using the technique described in our second semi-annual technical report. From the results of these measurements it is apparent that the amount of mercury vapor in the cell depends on the temperature, even at temperatures well above the temperature at which the cell was cut off. Measurements on mercury only cells show that little or no mercury is evolved from the quartz walls, thus the adsorption of mercuryonto the thallium is rather marked and temperature dependent. These results make the direct comparison of a mercury only cell with a mercury-thallium cell of questionable meaning.

In order to circumvent the problem of the adsorption of mercury onto thallium in the cells, we rearranged our experimental equipment so as to simultaneously measure the line absorption of 2537 A radiation in the cell and the fluorescent radiation. The present experimental arrangement is described below.

The experimental cell, prepared by methods previously described, is placed in a furnace with a ceramic mask which defines the scattering geometry. The source, a "Pen-Ray" 11SC-1 lamp, is placed at the focus of a quartz lens. One monochromator is used to measure the absorption of 2537 A resonance radiation through the cell, while another monochromator measures the scattering from the cell, either resonance fluorescence or sensitized fluorescence. The source intensity is monitored by a photomultiplier with

a narrow band filter to eliminate all but the 2537 A radiation. The calibration of the absorption and scattering measurements is made with a cell containing an excess of mercury only. With the main body of the cell at a fixed temperature in the 500°C to 800°C range the temperature of the cell side arm is reduced to liquid nitrogen temperatures, using a quartz cooling cell, and the transmission and scattering of the empty cell is recorded. The temperature of the side arm is then varied over a range of 0°C to 40°C and the absorption and scattering at each number density, which can be calculated from the vapor pressure of mercury and the effusion relation, is recorded. The percentage absorption and the scattering intensity is then plotted as a function of mercury number density at each main cell temperature.

For each cell containing mercury and thallium the above measurements are repeted, first the side arm temperature is reduced to liquid nitrogen temperature and the absorption and scattering of the empty cell is obtained. The cell temperature is then varied over the range 500°C to 800°C and the side arm is maintained 50°C lower in temperature than the main body of the cell to prevent condensation on the walls of the main cell body. At each temperature the percent absorption of the cell for 2537 A radiation is recorded and the intensity of scattering of 2537 A radiation and thallium sensitized fluorescence lines are recorded.

The analysis of the data is best described in terms of the following equations.

For two cells containing identical number densities, n_1, of mercury atoms at the same temperature, one having added thallium atoms at a number density n_4, and for a constant rate of excitation to the 6^3P_1 state we have the equation relating the number density of excited atoms in the

two cells as,

$$n_2/\tau + 2\, n_1 n_2 \sigma_{23}^2 \sqrt{2\pi RT\left(\frac{2}{m_1}\right)} =$$

$$n_2'/\tau + 2\, n_1 n_2' \sigma_{23}^2 \sqrt{2\pi RT\left(\frac{2}{m_1}\right)} +$$

$$2n_2' n_4 \sigma_{4T}^2 \sqrt{2\pi RT\left[\left(\frac{1}{m_1}\right)+\left(\frac{1}{m_2}\right)\right]}$$

where:

n_1 = number density of ground state mercury atoms,

n_2 = number density of excited mercury atoms in mercury only cell,

n_2' = number density of excited mercury atoms in a mercury-thallium cell,

n_4 = number density of ground state thallium atoms,

τ = life time of mercury 6^3P_1 state,

σ_{23}^2 = cross section for non-radiative transfer of mercury from 6^3P_1 state to the 6^3P_o state on collision with ground state mercury atoms,

σ_{4T}^2 = cross section for excitation of thallium from the ground state in collision with an excited mercury atom.

At any fixed temperature the intensity of resonance fluorescence radiation for the number density ranges encountered in this experiment is directly proportional to the number density of mercury atoms in the 6^3P_1 state. Thus we may write, $(n_2'/n_2-n_2') = (I'/I-I')$, where I = intensity of resonance fluorescence in mercury only cell and, I' = intensity of resonance fluorescence in a mercury-thallium cell.

The procedure for determining the total quenching cross-section is then:

(a) From the absorption data on the mercury only cell and a mercury-thallium cell at the same temperature determine the mercury number density in

the mercury-thallium cell.

(b) From the number density of mercury atoms in the cell and the data on the mercury only cell determine the expected scattering, I, at each temperature.

(c) Correction for slight changes in geometry between the cells and correction for the transmission of the windows will be a simple multiplicative constant which can be determined at low temperatures, where there is not enough thallium vapor to give any appreciable quenching; thus the scattering I' can be determined.

If the ratio (I'/I-I') at constant n_4 is plotted as a function of n_1, the number density of ground state mercury atoms, then both σ^2_{23} and σ^2_{4T} can be obtained from the slope and intercept of the resulting line. If $\sigma^2_{23}/\sigma^2_{4T}$ is small then the equation for σ^2_{4T} is,

$$\sigma^2_{4T} = \frac{I - I'}{I'} \qquad \frac{1}{n_4 \ \tau\sqrt{8\pi RT(1/m_1 + 1/m_2)}} ,$$

which can be used to find approximate cross sections. If the cross sections as computed from the preceeding equation are independent of n_1, over a range of n_1 values, then σ^2_{23} is negligible and the results from this approximate equation are valid.

At present only one complete set of data have been obtained. These data were for a cell having a mercury density in the range 0.4×10^{14} to 0.5×10^{14} atoms/cm^3 and thallium densitities ranging from $.15 \times 10^{14}$ to 50×10^{14} atoms/cm^3.

The crosssection results of a single run on this cell are tabulated below.

T°K	This method $\sigma^2_{4T}(\times 10^{16} cm^2)$	Prev. results $\sigma^2_{4T}(\times 10^{16} cm^2)$
746	5520 ± 5000	
773		indeterminate
867	1330 ± 590	
873		360 ± 50
970	280 ± 84	
973		260 ± 40
1068	36 ± 14	
1073		150 ± 40

It is apparent that the method we used for our previous measurements is more **reproducible**, however the number density of the mercury in that experiment was not well determined and the results may thus be considerably in error. The present method can be improved by (a) repeted measurements on the same cell, and (b) increased accuracy of temperature control.

We plan to continue this kind of measurement for all the cells we have. It is anticipated that these results will be obtained within the next quarter. When we have sufficient data on cross sections over a wider range of mercury densities we will analyze the results for the self quenching cross section σ^2_{23}.